

N64-26074

Code Name  
Cat 19

# Visible Absorption Spectra of Cadmium in Cadmium Halides and Lead Chloride and in Lead Bromide

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(Received 6 January 1964)

**R**EAGENT-grade materials were kept in a vacuum drying oven at 200°C for several days and then melted and filtered through Pyrex glass wool. The

TABLE I. Visible absorption maxima for cadmium and lead salts and metal mixtures.

Salt	$\lambda$ ( $\mu$ )	$T$ (°C)
CdCl <sub>2</sub>	0.360	588
CdBr <sub>2</sub>	0.500	600
CdI <sub>2</sub>	0.540	405
Cd-CdCl <sub>2</sub>	0.455	573
	0.455	593
	0.45-0.55	618
Cd-CdBr <sub>2</sub>	0.605	605
Cd-CdI <sub>2</sub>	0.665	390, 410
PbCl <sub>2</sub>	0.439	521
PbBr <sub>2</sub>	0.521	393
Pb-PbCl <sub>2</sub>	0.627	550
Pb-PbBr <sub>2</sub>	0.692	450

lead and cadmium metals had less than 1% impurity and were used without further purification.

Measurements in the visible and infrared were made using a Model 13 Perkin-Elmer spectrophotometer. The platinum screen technique was used to obtain data in the infrared.<sup>1</sup> In the visible, the reference and sample cells were made from 8-mm Pyrex tubing. The systems containing cadmium in cadmium halides were evacuated

and sealed. No such precautions were taken with the lead-lead halides, since saturated solutions were formed in which excess metal was always present.

The data obtained are reported in Table I and in Figs. 1 and 2. No specific infrared absorption bands were observed to 15  $\mu$  either in the pure salts or in the metal-salt mixtures. As in the case of the pure salts the effect of temperature on the visible metal-salt bands was initially to broaden the band and then shift the peak position to lower energies (longer wavelengths). The splitting of the band, as observed in the case of Cd in CdCl<sub>2</sub>, a few degrees above the melting point is analogous to the splitting that occurs in the spectra of crystals when the absorbing species can have more than one orientation in the lattice. As the temperature is raised, the band broadens and the split is not seen.

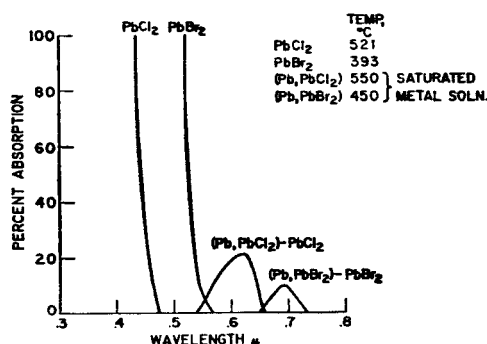
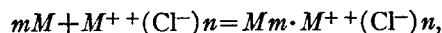


FIG. 2. Visible absorption spectra of PbCl<sub>2</sub>, PbBr<sub>2</sub>, and Pb in PbCl<sub>2</sub>, PbBr<sub>2</sub>.

The fact that there is not an absorption continuum in the visible indicates that the closely spaced energy levels typical of the metallic state are not present. If the cadmium and lead were in solution as neutral metal atoms, then the spectra might be considered as analogous to the vapor state and would center about some mean position rather than show such a distinct shift as a result of a change in anion. The data suggest therefore that the absorption process is a result of a charge transfer mechanism from the metal atom to the cation. Since the observed spectra show a distinct shift with the change in anion, it appears that the charge transfer process involves the reaction



where  $m$  is probably 1 or 2. Associated complexes have been suggested as a result of cryoscopic measurements.<sup>2</sup> In accordance with these assumptions, the fact that lead is less soluble in its halides than cadmium metal in its corresponding halides may be due in part to the fact that fewer  $p$  states in the lead ion are available to the electrons of the metal-atom donor.

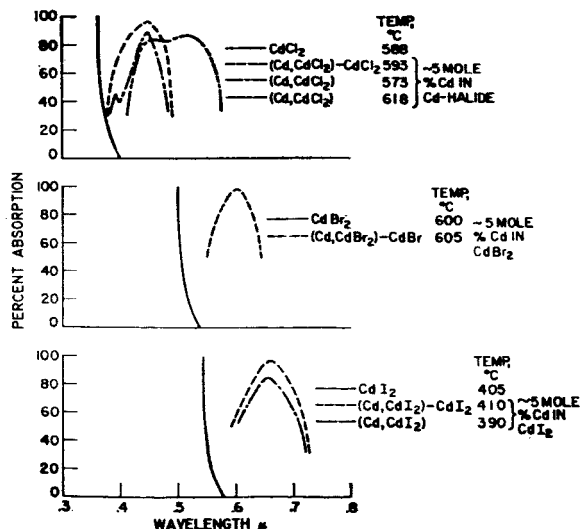


FIG. 1. Visible absorption spectra of cadmium halides and cadmium in cadmium halides.

<sup>1</sup> J. Greenberg and L. Hallgren, J. Chem. Phys. **33**, 900 (1960).

<sup>2</sup> L. E. Topol and A. L. Landis, J. Am. Chem. Soc. **82**, 6291 (1960).